Luminescent Magnets: Hybrid Supraparticles of a Lanthanide-based MOF and Ferromagnetic Iron Oxide by Assembly in a Droplet via Spray-drying

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Electronic Supplementary Information (ESI)

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ESI Summary:

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Supporting Video V3: A powder of hybrid supraparticles can be drawn over a surface by a magnet
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Supporting Video V1: Hybrid supraparticles show remarkable magnetic separation in daylight

Supporting Video V2: Hybrid supraparticles in water show strong luminescence under UV-light and can magnetically be separated as a whole.

Supporting Video V3: A powder of hybrid supraparticles can be drawn over a surface by a magnet. As the process is demonstrated under UV-light, the complete uniformity / homogeneity of the hybrid is visible, as even the tiniest bit of powder sample behaves magnetically and *at the same* time is strongly luminescent.



Figure S1. SEM of the selected FIONs used.



Figure S2. SEM of the obtained MOFFIOS products depending on the mass-related MOF:FION

ratio a 1-2) 1:3; b 1-2) 3:1 (1: overview; 2: detail).



Figure S3. Recorded powder X-ray diffraction patterns of spray-dried FION (brown), $_{\infty}$ [Eu₂(BDC)₃(H₂O)₄] synthesized by spray-drying (dark orange, "*fire*") and MOFFIOS with a MOF:FION ratio of 50:50 (red) in comparison to the diffraction patterns of magnetite^[1] (black) and $_{\infty}$ [Tb₂(BDC)₃(H₂O)₄]^[2] (light orange) both simulated from single crystal X-ray diffraction data. The Tb containing MOF is isotypic to the synthesized Eu containing MOF.



Figure S4. Single data points of photoluminescence quantification measurement ($\lambda_{em} = 617$ nm).



Figure S5. Absorption spectrum of a 2.2 wt-% dispersion of spray-dried FION.

Table S1. Correspondent amounts for each weight ratio used for spray-dry preparation of theMOFFIOS hybrids.

RATIO		Mass [mg]		MOF precursors mass	
				[mg]	
FION	MOF	FION	MOF	Na ₂ BDC	EuCl ₃ ·6H ₂ O
0.90	0.10	270	30	23.7	27.6
0.75	0.25	225	225	59.4	69.0
0.50	0.5	150	150	118.7	138.0
0.25	0.75	75	225	178.1	207.0
0.10	0.90	30	270	213.7	248.4

The calculated amounts of the FIONs and MOF precursors were calculated according to an initial 2.9 wt % FION dispersion, to yield 300 mg of final hybrid compound.

Table S2. Equivalents of contained $_{\infty}[Eu_2(BDC)_3(H_2O)_4]$ (MOF) and ferromagnetic iron oxide nanoparticles (FIONs) in spray-dried hybrid particles, as well as the corresponding fit parameters for the determination of the overall emission intensity decay. Each recorded decay was fitted with a monoexponential function $I_t = A + B \cdot exp(-t/\tau)$, where I_t stands for the intensity of the emission following the excitation pulse after a certain time interval t. A describes a baseline factor, B the pre-exponential factor and τ the luminescence lifetime. The fit quality was evaluated by χ^2 value.

Equivalents	Equivalents	Fit parameters					
MOF	FIONs	А	В	τ [ms]	χ^2		
1	0	1.17(8)	9893(6)	0.4457(3)	1.08		
0.9	0.1	2.4(1)	9868(6)	0.4528(3)	1.12		
0.5	0.5	1.78(9)	10075(6)	0.4461(3)	1.04		
0.1	0.9	3.0(1)	9695(6)	0.4257(3)	1.15		

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